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BATCH PROCESSING WITH THE RADIOIODINE LASER INDUCED-FLUORESCENC--ETC(U)
AUG 80 J R MCDONALD, A P BARONAVSKI
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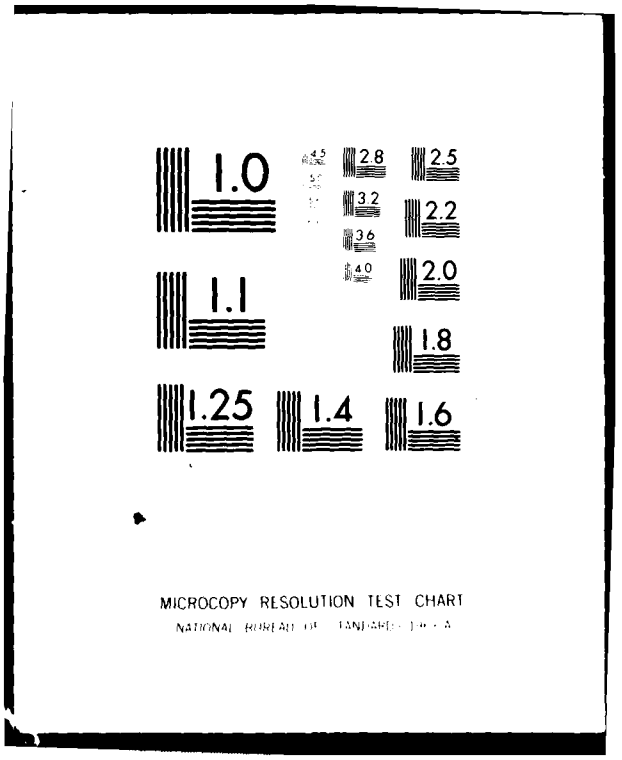
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The Chemistry Division of the Naval Research Laboratory in cooperation with the Department of Energy is carrying out research related to the detection and monitoring of airborne I_2^{129}. Methods for conversion of alkyl Iodides and HI to I_2 have been quantitatively evaluated for use in batch processing. Scrubbing properties of silver zeolites in terms of their affinity for I_2 and NO_2 and chemical and thermal desorption curves have been studies and evaluated for use in batch processing.

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BATCH PROCESSING WITH THE RADIOIODINE LASER INDUCED-FLUORESCENCE DETECTOR

1.0 INTRODUCTION

Previous reports have described the conception, development, and testing of a radioiodine detector based upon laser-induced-fluorescence.[1,2] The prototype detector fabricated by Bendix, Environmental and Process Instruments Division was shown to have a detection sensitivity[2] of $\leq 10^{-10}$ g/cm^3 for iodine(129). Subsequent to the design planning development stage it became apparent that detection sensitivities of 10^{-14} g/cm^3 were required and that these measurements must be carried out in the presence of 0.1 - 0.3% of NO_2 in the effluent off-gas. Therefore, in FY-79 studies were undertaken to convert the prototype detector for batch processing operation in which (1) the iodine in the effluent would be concentrated and (2) the iodine in the effluent would be separated from the high levels of the NO_2 interferrent.

Two techniques were investigated:

(1) scrubbing and concentrating on charcoal adsorbent; and

(2) scrubbing on Ag-zeolite (silver mordenite) followed by thermal desorption or stripping in H_2.

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Charcoal adsorbants were shown to be unsatisfactory because they have similar adsorption and desorption isotherms for I_2 and NO_2. The study of thermal desorption of I_2 from several classes of zeolites was shown to be impractical. Desorption of I_2 does not occur except at a temperature which leads to structural collapse of the zeolite. This desorption is accompanied by a release of AgI which appears at the detector as an aerosol, rendering the detector unusable.

Stripping of iodine (HI) from Ag-zeolites has been claimed to be effective[3] using H_2 at moderate temperatures. This stripping step then requires the subsequent conversion of HI to molecular iodine for measurement by the detector. Several cataysts were investigated for the reduction step of HI to I_2, and metallic gold[2] was determined to be the best. Studies near the end of FY-79 showed that the generation of I_2 from HI in this step was feasible. However, problems were encountered in the conversion process due to an apparent poisoning of the gold catalyst after a short period of time.

Subsequently, studies by ourselves and conversations with Lee Burger of Battelle-Northwest led us to believe that the poisoning of the gold catalyst likely resulted from depositing of silica on the gold surface of the catalyst. Several lines of investigation have been pursued during the first part of FY-80 with respect to conversion of the radioiodine detector for batch processing. Specifically, we have addressed the following:

(1) Can the iodine stripping step from the Ag-Zeolite be carried out using CH_4? Such a process would be expected to yield CH_3I whose subsequent conversion to I_2 is efficient and well understood. These studies were independently carried out by ourselves and by Burger.

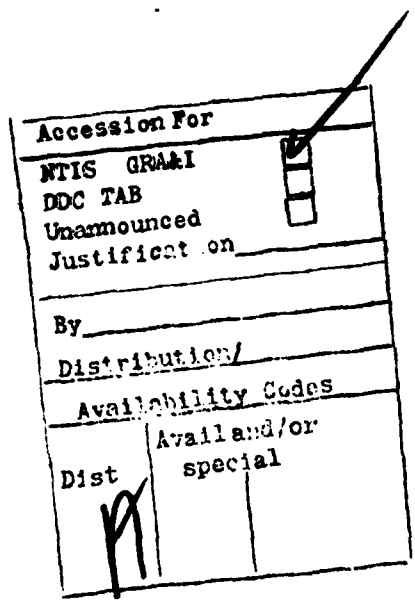
(2) Can the poisoning of the Au catalyst be avoided by eliminating the silica tube in which the reaction is run?

(3) Can the zeolite be demonstrated to independently scrub iodine while rejecting NO_2?

(4) Are the zeolites efficient and reproducible as concentrating media for iodine and can the iodine be recovered efficiently and reproducibly by stripping with CH_4 or H_2?

(5) What is the efficiency of the overall stripping and recovery steps and what is the detection sensitivity for iodine in the ultimate carrier gas?

Each of these areas have been studied and answers are now available for the questions posed above.



2.0 RESULTS

2.1 I_2 Scrubbing on Ag-Zeolite - Followed by CH_4 Stripping

Since it is documented that iodine can be stripped from silver mordenite in an H_2 stream at moderate temperature[3] an investigation was carried out using CH_4 as a possible desorbing agent. The methane would be expected to yield CH_3I as a primary product in the desorption step. Generation of CH_3I is preferred to HI because the conversion to molecular iodine is quantitative and takes place under mild temperature conditions without the aid of catalysts.

In a typical experiment 28.8 μg of I_2(127) was deposited on silver mordenite in the manner described previously[2]. The loaded zeolite is then purged in a counter current flow of CH_4. The effluent passes through the quartz oven routinely used for conversion of CH_3I to I_2 and subsequently through the iodine detector cell. No detectible I_2 signals are observed for temperatures $\leq 620^{\circ}C$. Heating above this temperature leads to collapse of the zeolite structure with subsequent release of AgI. The AgI is then partially pyrolyzed in the CH_4 yielding CH_3I, I_2, HI and copious particulates. The scattered light signal from the particulates overwhelms the fluorescence signals from I_2.

It is apparent that CH_4 will not significantly desorb iodine from silver mordenite at temperatures below the collapsing point of the zeolite structure. Subsequent to these

experiments we learned that Lee Burger[4] had carried out similar experiments with results equivalent to our observations. Because of the unsuitability of stripping iodine from zeolites with CH_4, studies returned to a consideration of the hydrogen stripping cycle.

2.2 Conversion of HI to I_2 Using Gold Catalysts.

It was reported[2] that metallic gold leads to effective conversion of HI by the process;

$$2HI \xrightarrow[1000^{\circ}C]{\text{gold}} H_2 + I_2.$$

The problem with this step was an apparent poisoning of the gold catalyst after a short period of operation. On the assumption[4] that vaporized silica deposits on the gold surface were responsible for this behavior, alumina carrier tubes were purchased and installed in the experimental setup previously described.[2]

The alumina tube furnace (with and i.d. of 5mm) has an active heated length of 5cm. The gold catalyst, 400μm wire, ∿15cm long was coiled in a spiral to fit inside the alumina tube. The length of the coil was ∿2.5 cm and was located at the center of the heated furnace.

Samples of HI in helium 1:1566 were passed through the catalyst oven at 982°C. The temperature was maintained below the melting point of gold. When the gold melts in the alumina tubes it does not wet the surface but coalesces into

drops reducing the effective surface area. Experiments were carried out to determine:

(1) the linearity of the I_2 fluorescence signal as a function of concentration of HI;

(2) the long term stability of the I_2 fluorescence signal under constant experimental conditions;

(3) the linearity of the I_2 fluorescence signal as a function of flow rate or residence time in the oven; and

(4) the conversion efficiency as a function of furnace temperature.

2.2.1 The HI/He mix was run through the furnace at 982°C at a flow of 45 cm^3/min for a period of time required to obtain a constant signal. Then additional He was valved into the flow prior to the furnace. The monitored fluorescence signal from I_2 varied linearly with HI concentration (within 5%) for all dilutions studied at this flow rate and temperature. This indicates that the system response is linear in concentration for HI concentrations up to 0.6% HI in He.

2.2.2 In experiments using the same catalyst and tube furnace setup, constant I_2 fluorescence signals have been observed for time periods of > 12 hours. We have noted no evidence of catalyst poisoning in alumina tubes in any of these experiments. We have found, however, that it is necessary to purge the catalyst with pure He at $\sim$ 900°C before running new samples after periods of shut down to reproduce

the measured efficiency for conversion in the system. This apparent activation step poses no problem, however, in the use of the system.

2.2.3. Since the gold catalyst wire has an effective coiled length of ∿2.5cm it is necessary to consider the total amount of time at a given flow rate that the HI gas mixture is in contact with the catalyst. This will be referred to as the characteristic residence time, (T_r). Tests were conducted at three temperatures as a function of flow rate of the 1:1566 HI:He to determine the flow conditions which would produce residence times adequate for equilibrium conversion of the HI to I_2. This is an important constraint because if the signal depends upon the flow rate it will not be possible to easily calibrate the measured signal against concentration. Figure 1 shows a plot of measured I_2 signal as a function of residence time on the catalyst for three different temperatures.

It is apparent that between 980 and 1040°C a gas residence time of > 8 msec is required for the conversion to I_2 to reach an equilibrium. At a lower temperature of 925°C, the required residence time has nearly doubled over that at the maximum of 1040° usable for gold. Thus the use of lower furnace temperatures requires either a lower flow rate or an extended active length for the catalyst furnace. Under our present experimental conditions, at 982°C a flow rate of 50 ml/min results in flow rate independent signals.

It is an interesting observation that the maximum flow rate independent signal attainable seems to be nearly independent of temperature in the range of 925-1040°C. The equilibrium expressions[2] predict that conversion efficiency to $I_2 + H_2$ increases with temperature. The results shown in Figure 1 are consistent with either a very slowly changing equilibrium constant with temperature or with near quantitative conversion to I_2. The equilibrium constant data in the literature[2] is available for temperatures much lower than these and extrapolations to these temperatures may or may not be valid.

2.2.4 It is possible to evaluate an "effective" conversion efficiency by a different technique. Using the CH_3I permeation tube with a helium flow and the quartz oven at 1000°C gives quantitative conversion of CH_3I to I_2. Under these conditions our measured detector sensitivity for iodine(127) is 1.1±0.1 namp ng^{-1} ml. From the measurements using HI:He and the gold catalyst we measure a detector response of 0.39 namp ng^{-1} ml. In the absence of other effects this corresponds to a conversion efficiency of 35%. This measurement is flow independent (at $\leq$ 50 ml/min and 982°C). Moreover, the conversion is only slightly if at all temperature dependent in the 925-1040°C range. These measurements assume an identical fluorescence signal from I_2 generated from CH_3I and HI. The actual fluorescence signal will depend upon the other gases present. The quenching of I_2

fluorescence by HI, I_2 and H_2 will be different than the similiar experiments using CH_3I pyrolysis. It is possible that the conversion is somewhat higher than 35% and that we measure an apparent conversion of 35% and because of these quenching effects. In reality this is unimportant since the measured calibration and detector response automatically takes these effects into account.

2.2.5. If one were to liberate the iodine from the zeolite in an H_2 stream and subsequently convert HI to I_2 in this stream the final measurement would most conveniently be made in the H_2 flow stream. As we noted above the I_2 signal measured depends upon the carrier gas because of the varying quenching rate of I_2 fluorescence with collision partner. Helium has been used as the carrier gas in our previous measurements on iodine(127) because it is the least efficient quencher and gives the largest fluorescence signals. Using the CH_3I premeation tube and both He and H_2 carrier gas in several experiments we find that the fluorescence quenching efficiency of H_2 is 18.67 times larger than He for the I_2 fluorescence.

These measurements now allow us to determine the amount of I_2 stripped from the Ag-zeolite in a typical scrubbing experiment. In an experiment the following correction factor can be applied:

$$\frac{\text{Integral of Signal(namp-ml)}}{1.1 \text{ namp ng}^{-1}\text{ml}} \times \frac{1}{0.35} \times 18.67.$$

Dividing this factor by the known amount of I_2 deposited on the zeolite will give a total efficiency for the scrubbing and stripping process on the Ag zeolite.

2.2.6. Scrubbing and Stripping of NO_2 on Silver Zeolite

A mixture of 0.3% NO_2 in He was made up and passed through the Ag zeolite bed described above at room temperature. By purging the zeolite bed between 300 and 500°C we find that:

(1) a portion of the NO_2 is adsorbed by the zeolite;

(2) the NO_2 adsorbed on the zeolite is removed in the counter current He purge between 300 and 500°C.

These results are shown in Figure 2. Also shown in Figure 2 is the subsequent purge of the zeolite bed with H_2 gas following the He purge. It is apparent that the adsorbed NO_2 is quantitatively removed from the zeolite under conditions which adsorbed I_2 remains firmly in place.

Given our detector response for NO_2 in He of 0.09 namp μg^{-1} ml, we find that, for the loadings used, 88% of the NO_2 is adsorbed and subsequently quantitatively stripped in He at $\leq$500°C. Since I_2 does not desorb at these temperatures the thermal desorption of NO_2 in He at 500°C provides the means of separating the NO_2 and I_2 from each other in the

effluent gas samples. Many repetitions of the NO_2 scrubbing and stripping cycles show that this step is highly reproducible and independent of the prior history of the Ag-zeolite scrubbing bed. It is interesting to note that the NO_2 desorption step correlates with the decomposition temperature of $AgNO_3$ to $AgO + NO_2$. It seems likely that the NO_2 which is initially scrubbed onto the silver zeolite probably is adsorbed at AgO sites to form $AgNO_3$ and is subsequently liberated when the $AgNO_3$ decomposes.

2.2.7 Stripping Iodine from Ag-Zeolite with Hydrogen

In a typical experiment molecular iodine is deposited on the Ag-zeolite in a controlled manner following conversion of CH_3I in the quartz furnace to I_2. This allows precisely measured samples to be metered onto the adsorbant. H_2 gas is used in a countercurrent flow to strip the iodine from the adsorbant bed. The resulting HI in the H_2 stream is passed through the gold catalyst tube furnace and subsequently through the fluorescence detection cell. Each of the steps in this process has been thoroughly investigated and is reproducible and understood.

Figure 3 shows a desorption curve, plotted as I_2 fluorescence intensity for the H_2 stripping process. Integration of the fluorescence signal and correction for the detector response and HI conversion efficiency as described above indicates a near unit efficiency for the

iodine stripping process in hydrogen. The chemical stripping process and the temperature dependence of the desorption is much as might be expected from the reported data by Burger for the similar process using a much larger zeolite bed and higher iodine loadings.

Unfortunately, we have found the process as shown in Figure 3 to be highly nonreproducible. After many experimental runs to evaluate this chemical desorption step we have made the following observations:

1. The temperature dependence of the desorption is highly variable. Under some runs it has not been possible to desorb the I_2 below the collapse temperature of the zeolite;

2. The integrated I_2 signal (which is a measure of the stripping efficiency) is variable from run to run;

3. The behavior of the zeolite in the desorption step appears to be dependent upon the history of the zeolite in prior runs. The zeolite appears to be sensitive to prior exposure to NO_2;

4. It has not been possible to define a set of operating conditions which will give a predicitable desorption behavior for I_2 in H_2.

At the present time we are at a loss to explain the observed behavior of the zeolite in this stripping step. This is particularly bothersome considering the predictability and repeatability of the NO_2 deposit and desorption process which also apparently involves a chemical reaction and chemical decomposition step. We are currently re-

considering our results and observations involving the hydrogen stripping step. We would welcome any comments or suggestions from other workers in the industry which might lead to an understanding of the process and allow its use in this critical scrubbing and separation step.

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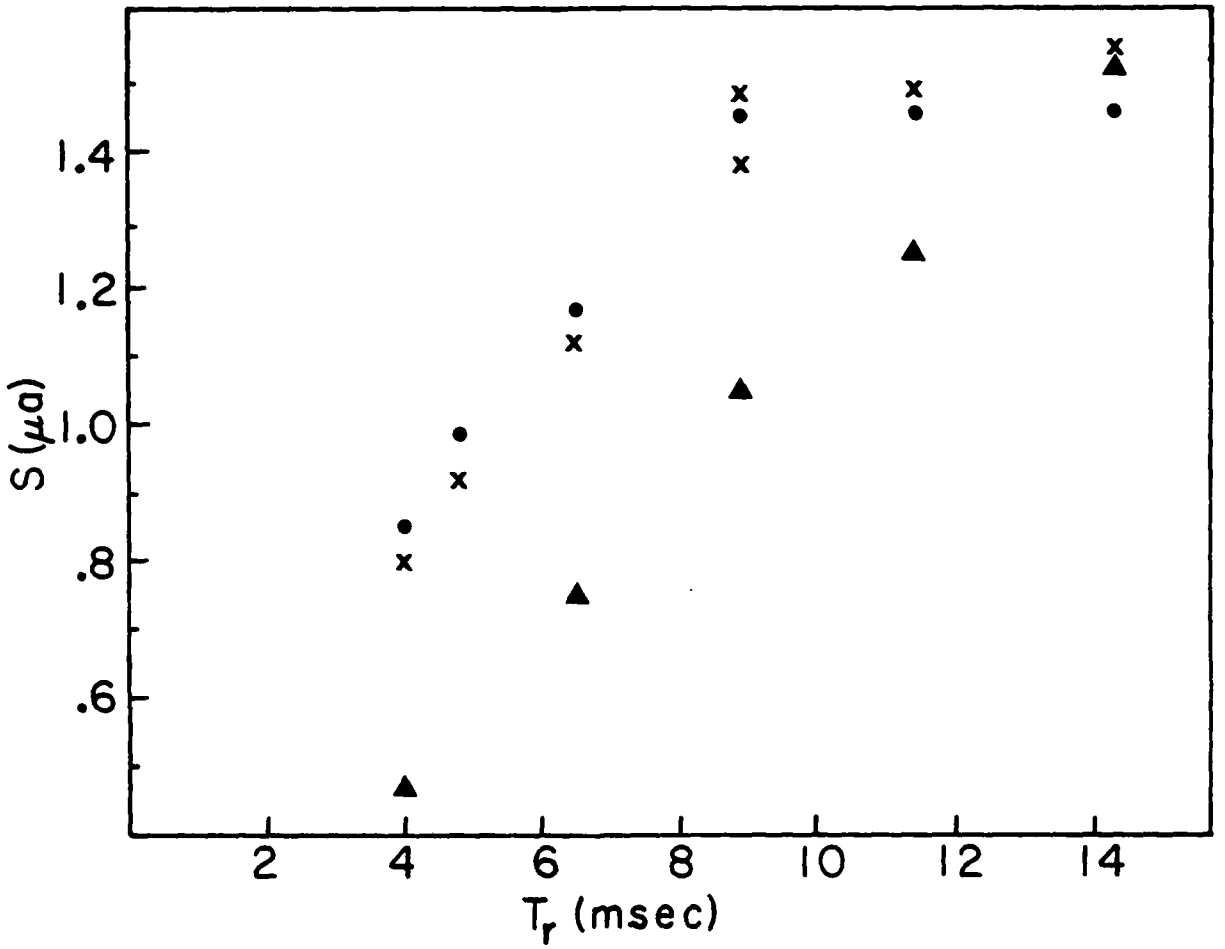

Fig. 1 — A plot of the I_2 fluorescence signal from the conversion $2HI \rightarrow H_2 + I_2$ over the gold catalyst as a function of the residence time of the gases on the catalyst. (●) at 982°C; (X) at 1038°C; (▲) at 927°C.

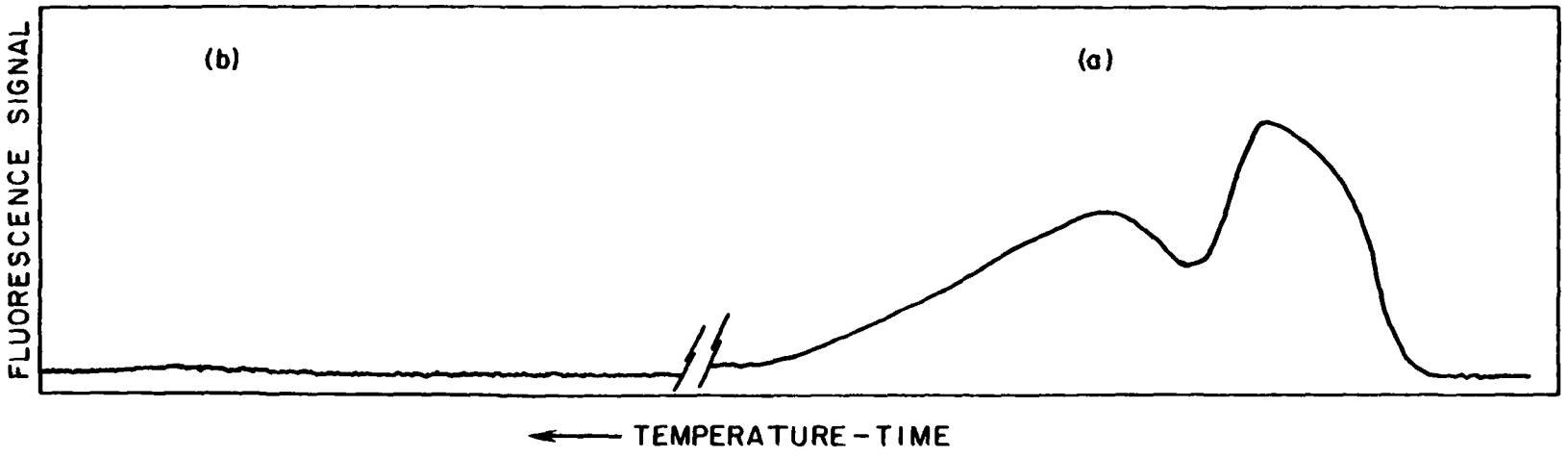

Fig. 2 — Temperature-time histogram for the desorption of NO_2 from silver mordenite. (a) corresponds stripping from 93°C to 538°C in He. (b) corresponds to the same temperature range for subsequent stripping of the same sample using He and indicates that the desorption on NO_2 in a He stream is complete.

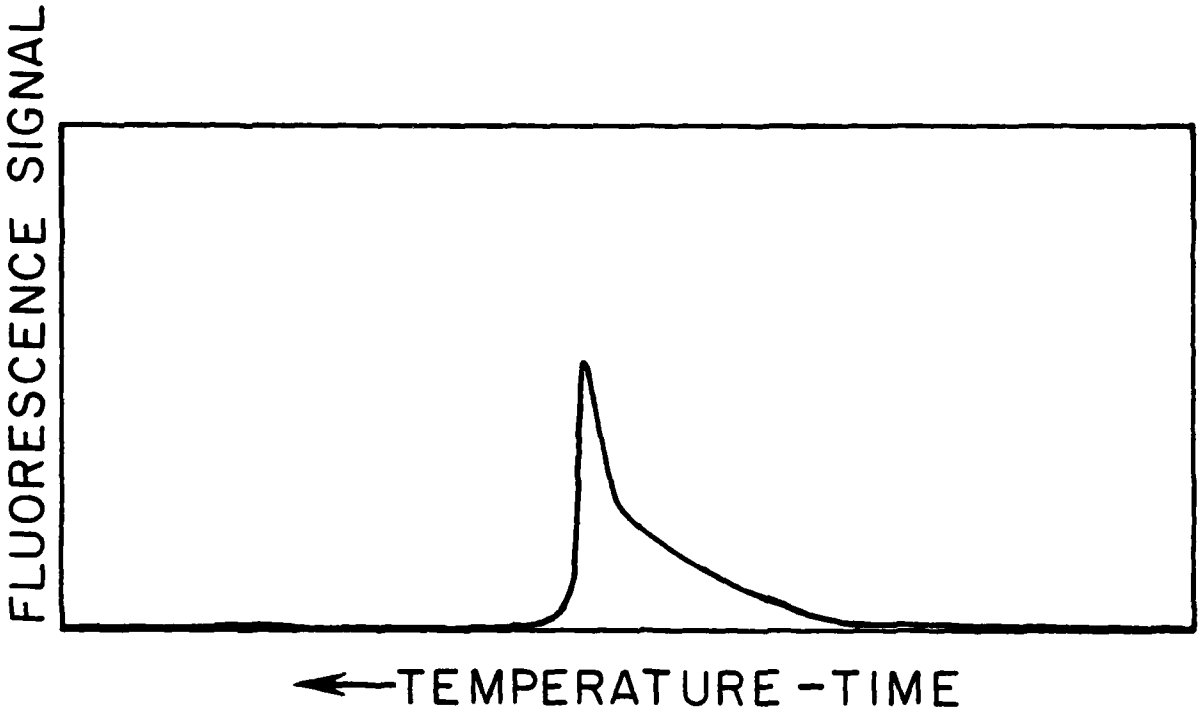

Fig. 3 — Temperature-time histogram for the desorption of I_2 from silver zeolite from 93°C to 538°C. See text for details.